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Abstract

A, kinetic study of the pyrolysis of toluene by a flow technique has been made, and assuming Szwarc's mechanism, two activation energies (78.3 and 84 kcal/mole depending on the temperature range used) have been derived for the dissociation of the (C-H) bond in the methyl group of toluene. The lower value agrees quite well with Szwarc's, and the higher value turns out to be approximately the average of 77.5 and 89.9. The results of this research suggest 84 kcal/mole as the upper limit for the activation energy.

Keywords

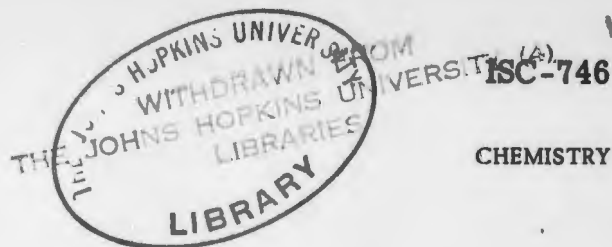
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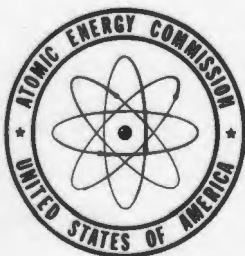
UNITED STATES ATOMIC ENERGY COMMISSION

THE (C-H) BOND DISSOCIATION ENERGY IN
THE METHYL GROUP OF TOLUENE

By
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F. R. Duke
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March 1956

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Technical Information Service Extension, Oak Ridge, Tenn.

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F. H. Spedding, Director of Ames Laboratory.

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ABSTRACT

A kinetic study of the pyrolysis of toluene by a flow technique has been made, and assuming Szwarc's mechanism, two activation energies (78.3 and 84 kcal/mole depending on the temperature range used) have been derived for the dissociation of the (C-H) bond in the methyl group of toluene. The lower value agrees quite well with Szwarc's, and the higher value turns out to be approximately the average of 77.5 and 89.9. The results of this research suggest 84 kcal/mole as the upper limit for the activation energy.

The ultraviolet spectra of the solid decomposition product indicated that the solid was not pure dibenzyl but probably contained small amounts of a compound possessing a diphenyl nucleus. The rate of formation of hydrogen and methane was found to be inhibited by small amounts of air, and the percentage of hydrogen was found to increase slightly with temperature. A detailed description of the apparatus and its operation is given.

The concept of group potential has been introduced to predict bond dissociation energies of carbon-hetero atom and carbon-carbon bonds.

INTRODUCTION

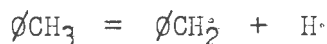
There exists some discrepancy in the literature regarding the (C-H) bond dissociation energy in the methyl group of toluene. Three methods have been employed to measure this quantity, kinetics of pyrolysis in a flow system, electron impact and bromination kinetics, and the values assigned thus far to the dissociation energy are approximately 78 and 90 kcal/mole. This research was undertaken to resolve the discrepancy, and the pyrolysis technique was employed to do so.

*This report is based on an M. S. thesis by Joseph Ignatius Genco, submitted March, 1956, to Iowa State College, Ames, Iowa. This work was done under contract with the Atomic Energy Commission

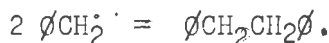
HISTORICAL

Jost and Muffling¹ were among the early investigators who studied the thermal decomposition of toluene semiquantitatively. They heated toluene to a temperature of 690°C in a static system and took pressure-time data from initial pressures of 100 mm and 300 mm of mercury. An analysis of their products indicated the presence of hydrogen but not methane.

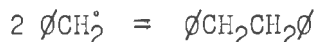
Szwarc² made a quantitative study of the thermal decomposition of toluene in a flow system from 738°C to 864°C and found hydrogen, methane, dibenzyl and benzene; no ethane, ethene or higher paraffins were observed. The number of moles of dibenzyl found was approximately equal to the number of moles of gas (hydrogen + methane), and the ratio of hydrogen to methane ($\sim 3/2$) was independent of temperature and contact time. Szwarc determined the activation energy (77.5 kcal/mole) for the decomposition of toluene and assumed this to be equal to the (C-H) bond dissociation energy in the methyl group. The mechanism he postulated is as follows:



and



Such a mechanism is not the only one which will give the experimental proportion of (hydrogen + methane) to dibenzyl. For example, the mechanism



will accomplish the same thing. Szwarc objected to the second mechanism on the basis that $D(\phi\text{-CH}_3) = 88.6$ kcal/mole (suggested by him) is too much greater than $D(\phi\text{CH}_2\text{-H})$. This point will be discussed later in this report.

Hentz and Burton³ irradiated toluene, mesitylene and ethylbenzene at a temperature of 150°C and pressures of 1-10 cm of mercury with a light source having a wave length of 2537 Å. The percentage composition of the gaseous products obtained is given in Table 1. If their postulate is correct; i.e., if the energy absorbed by the electrons in the benzene ring is transmitted mostly to the weakest bond in the molecule, then the results in Table 1 indicate that the (C-H) bond in the methyl group is weaker than the (C-C) bond between the methyl and phenyl groups of toluene.

Table 1

Gas Compositions from Photolysis of Aromatic Compounds^a

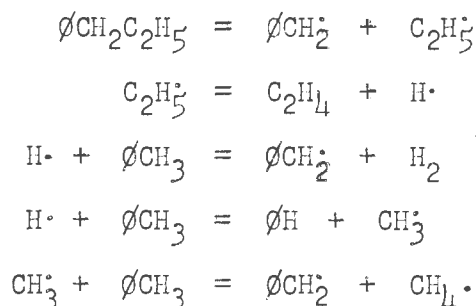
Compound	Percent Composition		
	H ₂	CH ₄	C ₂ H ₆ (approx)
Toluene	86	10.8	3.6
Mesitylene	84	8.7	7.0
Ethylbenzene	14	50	36

^aData taken from reference 3.

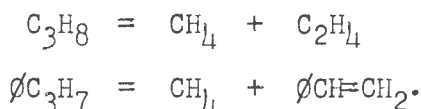
H. Blades, A. Blades and E. Steacie⁴ have also pyrolyzed toluene in an apparatus similar to that used by Szwarc, and their investigation covered the temperature range from about 857°C to 947°C. During their first pyrolysis run C₂ and C₄ hydrocarbons were obtained, but these disappeared after the toluene had been pyrolyzed about two or three times. They observed non-condensable gases consisting of 69% hydrogen and 31% methane, the ratio of which was independent of temperature and contact time. Benzene was found in quantities equal to that of methane, and the amount of dibenzyl found was less than that predicted by Szwarc's mechanism. In addition, some isomers of dimethyl diphenyl, styrene and anthracene have been identified. A plot of $\ln k$ versus $1/T$ for a constant contact time gave an activation energy of about 90 kcal/mole, but the authors were unwilling to commit themselves in saying that this is the dissociation energy for the (C-H) bond in question. They indicated that the rate constant changed with contact time and surface condition; however, the former effect could very easily be attributed to a high rate of flow and unattainment of temperature equilibrium.

A. Blades and E. Steacie⁵ pyrolyzed propylbenzene in the presence of 87% deuterated toluene to verify the mechanism for the decomposition of

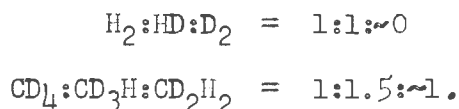
propylbenzene and toluene. As postulated by Szwarc the mechanism for the decomposition of propylbenzene in the presence of toluene is as follows:



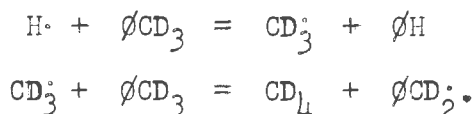
Blades and Steacie suggested that the compound might decompose similarly to propane by a molecular mechanism; i.e.,



The deuterated toluene consisted of 66% d₃, 29% d₂ and 5% d₁, and the experiment was performed at a contact time of 0.45 seconds, a pressure of 1.7 cm of mercury and temperature of 722°C. The toluene to propylbenzene ratio in the feed was 40/1. Under these conditions 30% of the propylbenzene decomposed, and the products obtained were found to be in the following ratio:

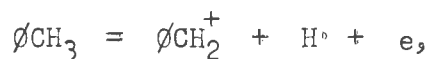


Normal benzene was found, but the presence of deuterated benzene was uncertain. On the basis of what they found Blades and Steacie concluded that the following process must take place.



Because a large percentage of H₂ was found they concluded that hydrogen was abstracted from the benzene ring. Unfortunately no mention was made of the ratio of total hydrogen to methane.

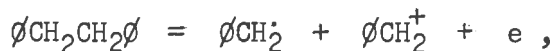
Schissler and Stevenson⁶ measured the (C-H) bond dissociation energy in the methyl group of toluene by electron impact and obtained a value of 77±3 kcal/mole. This method involves the determination of the appearance potentials of the benzyl ion from toluene and dibenzyl. The appearance potential of the benzyl ion in the particular process,



is defined in the following way:

$$A_1(\phi\text{CH}_2^+) = D(\phi\text{CH}_2\text{-H}) + I(\phi\text{CH}_2) , \quad (1)$$

and in the particular process,



it is defined thusly:

$$A_2(\phi\text{CH}_2^+) = D(\phi\text{CH}_2\text{-CH}_2\phi) + I(\phi\text{CH}_2) . \quad (2)$$

$I(\phi\text{CH}_2)$ is the ionization potential of ϕCH_2 . Subtraction of equation (1) from (2) yields



and the related thermochemical equation,

$$A_2 - A_1 = D(\phi\text{CH}_2\text{-CH}_2\phi) - D(\phi\text{CH}_2\text{-H}) . \quad (3)$$

The enthalpy change, ΔH_4 , for the reaction,



may be calculated from the heats of formation of dibenzyl, toluene and hydrogen atom. Subtraction of (4) from (3) yields the following chemical and thermochemical equations:



$$\Delta H_5 = (A_2 - A_1) - \Delta H_4 = D(\phi\text{CH}_2\text{-H}) .$$

Farmer, Henderson, McDowell and Lossing⁷ questioned the validity of the values, A_1 and A_2 , used by Schissler and Stevenson. They computed the ionization potential of the benzyl radical from the following equation:

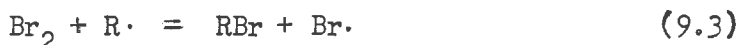
$$\begin{aligned} I(\phi\text{CH}_2) = & 2 A_1(\phi\text{CH}_2^+) - A_2(\phi\text{CH}_2^+) - 2 \Delta H_f(\phi\text{CH}_3) \\ & - \Delta H_f(\phi\text{CH}_2\text{CH}_2\phi) - 2 \Delta H_f(\text{H}) = 8.51 \text{ ev} , \end{aligned} \quad (6)$$

and compared its value with experimental ionization potentials derived from benzyl iodide (7.73 ev) and benzyl amine (7.81 ev), the average being given by $(7.76 \pm 0.08 \text{ ev})$. Indeed they do not agree. The expression given above may be derived in the following way:

$$\begin{aligned}
2 A_1 &= 2 D(\phi\text{CH}_2\text{-H}) + 2 I(\phi\text{CH}_2\dot{)} \\
- A_2 &= - D(\phi\text{CH}_2\text{-CH}_2\phi) - I(\phi\text{CH}_2\dot{)} \\
\hline
2 A_1 - A_2 &= 2 D(\phi\text{CH}_2\text{-H}) - D(\phi\text{CH}_2\text{-CH}_2\phi) + I(\phi\text{CH}_2\dot{)} \quad (7) \\
2 \Delta H_f(\phi\text{CH}_2\dot{)} &= 2 \Delta H_f(\phi\text{CH}_3) + 2 D(\phi\text{CH}_2\text{-H}) - 2 \Delta H_f(\text{H}) \\
2 \Delta H_f(\phi\text{CH}_2\dot{)} &= \Delta H_f(\phi\text{CH}_2)_2 + D(\phi\text{CH}_2\text{-CH}_2\phi) \\
\hline
2 D(\phi\text{CH}_2\text{-H}) - D(\phi\text{CH}_2\text{-CH}_2\phi) &= \Delta H_f(\phi\text{CH}_2)_2 - 2 \Delta H_f(\phi\text{CH}_3) \\
&\quad 2 \Delta H_f(\text{H}) \quad (8)
\end{aligned}$$

Substitution of equation (8) into (7) and rearrangement will yield equation (6).

Anderson, Scheraga and Van Artsdalen⁸ also measured the (C-H) bond dissociation energy from the kinetics of bromination of toluene. They assumed the photochemical bromination to take place in the following way:



M = any molecule present.

The rate law derived from the above mechanism is given by

$$-\frac{d(\text{Br}_2)}{dt} = \frac{k_2(\text{RH})}{1 + k_4} \frac{[\phi\text{I}_a/k_5(\text{M})]^{\frac{1}{2}}}{(\text{HBr})/k_3(\text{Br}_2)} \quad (10)$$

The symbols have the following significance:

- ϕ = absorbed effective light quanta
- I_a = intensity of absorbed light
- ϕI_a = $k_{\text{app}} \propto I_0(\text{Br}_2)$
- k_{app} = temperature independent apparatus constant
- α = absorption coefficient of Br_2
- I_0 = intensity of a given wave length of light
- () = concentration.

The photochemical reaction has been observed to follow the rate law,

$$-\frac{d(\text{Br}_2)}{dt} = \frac{k(\text{Br}_2)^{\frac{1}{2}}(\text{RH})^{\frac{1}{2}}}{1 + n(\text{HBr})/(\text{Br}_2)} \quad (11)$$

where n is the inhibition constant and temperature dependent. An examination of the two rate expressions will show that

$$n = k_4/k_3 ;$$

$k_5(\text{M})$ should be replaced by $k_5'(\text{Br}_2) + k_5''(\text{RH})$, but if RH is a more effective third body than Br_2 ; i.e., $k_5'' \gg k_5'$, and $(\text{RH}) > (\text{Br}_2)$ then the expression,

$$k_5(\text{M}) = k_5'(\text{Br}_2) + k_5''(\text{RH}) ,$$

becomes

$$k_5(\text{M}) = k_5''(\text{RH}) .$$

It is seen that $k = k_2(k_{\text{app}} \propto I_0/k_5)^{\frac{1}{2}}$. Anderson et al. determined the initial rate and used the equation,

$$-\frac{d(\text{Br}_2)}{dt} = k(\text{Br}_2)^{\frac{1}{2}}(\text{RH})^{\frac{1}{2}} \quad (12)$$

(RH) essentially constant

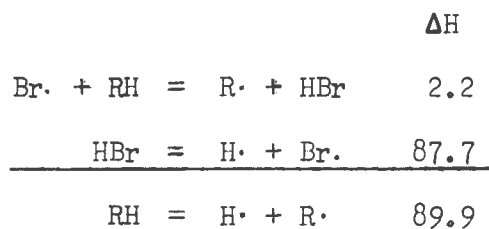
to calculate k . They determined k for different temperatures (82°C-132°C) and made a plot of $\log k$ versus $1/T$ to obtain an activation energy which was assigned to reaction (9.2). In order to do so they had to assume that k_5 (on the grounds that the activation energy for reaction (9.5) is zero) and $k_{\text{app}} \propto I_0$ are independent of temperature. The temperature dependent inhibition constant was determined from equation (11) in which the values of k found from the uninhibited reaction were used. In studying the reaction they added hydrogen bromide, maintained its partial pressure and that of toluene essentially constant and measured the initial rate with varying pressures of bromine. A plot of $\log n$ versus $1/T$ yielded an activation energy which was equated to the difference in activation energies of reactions (9.4) and (9.3) in compliance with the equation,

$$\log n = \log k_4/k_3 = \log A_4/A_3 - (E_4 - E_3)/2.3 RT.$$

The enthalpy for the reaction,



was calculated by assuming E_3 to be zero and taking the difference between the activation energies of reactions (9.2) and (9.4). When this value is combined with the heat of dissociation of hydrogen bromide the (C-H) bond dissociation energy is obtained in the following way:



Thus the (C-H) bond dissociation energy appears to be either 77.5 or 89.9 kcal/mole, and no rigorous proof has been given to prefer one or the other.

EXPERIMENTAL

A. Apparatus

The apparatus is shown in Figure 4; it is essentially the same as that used by Szwarc², but because the details of his apparatus were not given the essential parts will be discussed here. The mercury jet and diffusion pumps used in the apparatus were purchased from H. S. Martin and Company; catalog numbers (M-40130 and M-40131).

1. Outgassing system - Figure 1

This system is separate from the pyrolysis apparatus and is used to outgas and transfer toluene (in vacuum) into another vessel which can be weighed and connected to the pyrolysis apparatus. Except for simplifying modifications the system is equivalent to that described by Rossini, Mair and Streiff⁹. The funnel is used to pour toluene into the reservoir, but in this research calcium hydride was used in place of silica gel to remove moisture. The liter flask is a chamber into which the gas dissolved in the toluene may escape.

The procedure for outgassing and transferring toluene in a vacuum is as follows. Evacuate the entire system to less than 10^{-5} mm of mercury and close S-A, S-C and S-E (S=stopcock). Admit dry helium or nitrogen at a pressure of about 1-2 pounds per square inch greater than atmospheric into the system by opening S-D. Remove cap F, place the special funnel in the inlet of the reservoir and stop the gas flow. Pour toluene into the funnel (if silica gel is used Rossini et al. recommend cooling the hydrocarbon to 0°C before pouring). To hasten the flow of toluene open S-C slowly. After all the toluene has entered the reservoir start the flow of nitrogen and remove the funnel; replace cap F and close S-D and S-B. Freeze the toluene with liquid nitrogen and open S-B, S-C and S-E to remove the nitrogen; then, close S-E and lower the liquid nitrogen bath so as to just melt the toluene completely. Freeze once more and open S-E to remove the gases. Do this once more and repeat the following procedure about three times. Close S-B and melt the toluene completely. In the meantime evacuate the gas expansion chamber to about 10^{-5} mm of mercury or less. Close S-E and open S-B to allow the dissolved gases in the toluene to expand into the liter flask. Freeze the toluene, close S-B and evacuate the liter flask again.

In order to transfer the toluene from the reservoir to the receiver, close S-C and evacuate the line to a very low pressure. Close S-E, place a liquid nitrogen bath under the receiver, open S-A and S-B and allow the toluene in the reservoir to reach room temperature. The toluene will flow from the reservoir to the receiver under its own vapor pressure. When a sufficient amount of toluene has been collected close S-A and seal off the tubing at the point marked "glass seal".

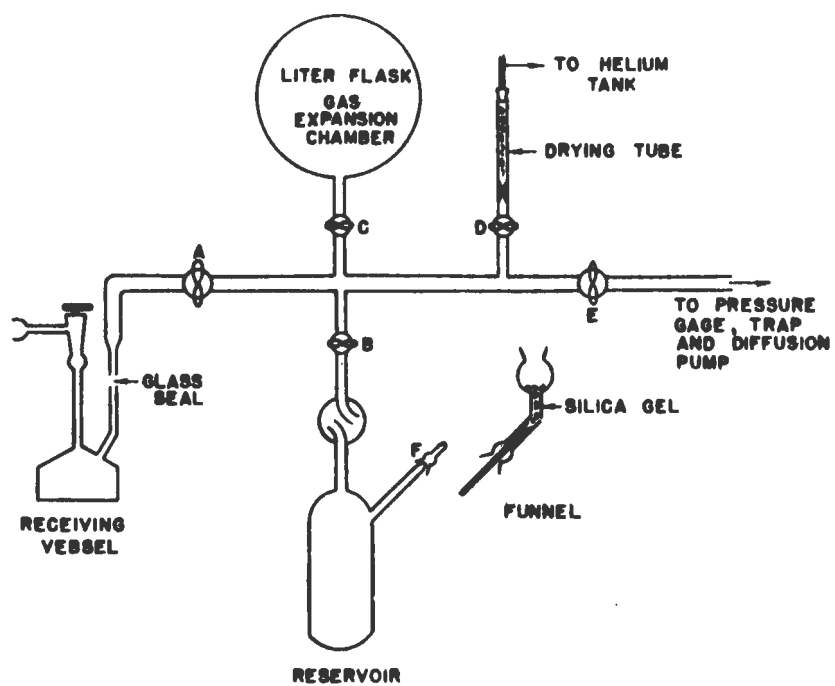


Figure 1. Outgassing and Vacuum Transfer System

2. Toluene reservoir and water bath

The first reservoir, being spherical, caused the pressure of the toluene in the reactor tube to decrease with time during a run. Since the vessel was usually only half filled the effect was attributed to the decreasing surface area from which toluene evaporated. To maintain the surface area of the liquid constant a cylindrical vessel was designed, but the pressure still decreased. This meant that the toluene was not being supplied with enough heat to maintain its temperature, and therefore its vapor pressure, constant. A check on thermal conductivities showed that glass is a better conductor than toluene by at least a factor of ten. Insertion of copper tubes in the liquid to distribute the heat throughout the toluene did not help. There was only one alternative left. The amount of heat transferred through a wall per unit time is proportional to the area of that wall, but since the level of toluene decreases during a run the effective surface area through which toluene must be heated also decreases. Thus it is seen that in order to maintain a constant rate of evaporation a constant rate of heat input must be supplied, and this condition will not be satisfied if the level of toluene decreases. To remedy the situation the reservoir was made cylindrical in shape with an outside diameter of 7.5 cm and vertical wall height of 3 cm. In this way the level of toluene did not change very much during any one particular run. This device gave satisfactory results. The largest and least variation of pressure in the runs made with this reservoir were ± 0.1 mm and ± 0.02 mm of mercury.

The water bath for the reservoir was usually kept constant to within about 0.05°C . It consisted of a three liter Dewar flask, an intermittent heater, a stirrer, a mercury thermoregulator and relay control system.

3. Quartz reactor tube - Figure 2

In the case of laminar flow, the equation for heat transfer by forced convection indicates that the temperature achieved by a fluid flowing through a tube which is at a uniform temperature depends on, among other important physical properties, the mass rate of flow and the length of the tube.¹⁰ If it is desirable to obtain good temperature equilibrium a long tube and low rates of flow should be used. A small diameter tube is preferred over a large one; unless, the rate of decomposition of a compound is extremely slow or wall effects become serious. For the same percentage decomposition a small diameter tube (small volume) will encourage a slower rate of flow and better temperature equilibrium. Also a small percentage decomposition is recommended because this will reduce the amount of side reactions taking place. The inlet and outlet tubes to the reaction chamber should be of small diameters to reduce the time spent by the gases in these zones and thereby reduce the amount of decomposition which could occur in the temperature gradient. The size of one of these tubes must not be so small as to produce a large pressure drop along it because the pressure of the gases in the reaction zone must be measured at a point remote from it. For this reason the outlet tube was made of a larger diameter than the inlet. The large bulge at the outlet was included to retard the gases and reduce the Bernoulli effect.

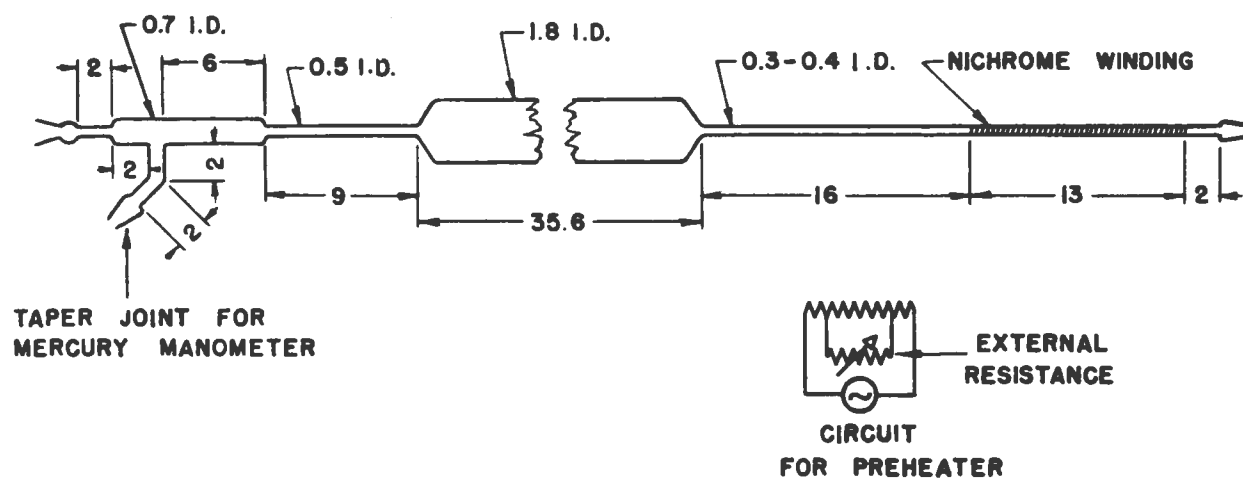


Figure 2. Reactor Tube and Preheater Circuit
(dimensions in cm)

4. Capillaries

A thin copper disc with a small hole drilled through the center of it was inserted at the standard taper joint of the inlet and outlet of the reactor tube to regulate the rate of flow of toluene. (See Figure 4 for details.) The sizes of capillaries used for different runs are given in Table 2. It was found that the inlet capillary was not as useful for controlling conditions of pressure, contact time and mass rate of flow as the outlet.

Table 2
Capillary Sizes

Runs	Diameter of Hole in Inches	
	Inlet	Outlet
III	0.073	0.043
IV	0.073	0.070
V	0.073	0.110
VI	0.0785	0.141
VII-XII, XVI-XVIII	0.0785	0.043
XV	0.120	0.073

5. Preheater

It was necessary to incorporate a preheater in the apparatus because the temperature of the main furnace cooled several degrees when toluene was sent through the reactor tube. Nichrome wire was wound directly on the inlet of the reactor tube as shown in Figure 2. After a layer of Alundum cement was put over the wire and allowed to dry, a chromel-alumel thermocouple was placed on top of it and a second layer of Alundum cement was applied. An insulator block $2\frac{1}{2}$ in. x $2\frac{1}{2}$ in. was slipped over the heater after the reactor tube was placed in the main furnace. The electrical circuit which was designed to produce a reasonably uniform temperature distribution in the preheater is also included in the figure.

6. Traps

During a run T_1 (T =trap) was immersed in a carbon dioxide-alcohol bath to collect solid and liquid decomposition products and most of the toluene, and T_3 and T_4 were immersed in liquid nitrogen baths to collect uncondensed toluene and C_2 and C_3 hydrocarbons. After the run the liquid contents of T_1 were vacuum distilled into T_2 to separate the solid products from toluene and benzene so that they can be weighed. This was done by placing a carbon dioxide-alcohol bath under T_2 and a salt-ice bath at about -15°C under T_1 .

7. Main furnace - Figure 3

An Alundum tube, 24 in. long, 1.5 in. I.D., 2 in. O.D., was used as the core upon which was wound nichrome wire, B. & S. Gauge #14, 0.158 ohms per foot, at ten turns per inch over the 18 in. center portion of the tube; grooves were cut into the Alundum to act as guides for the wire. Four taps were taken from the winding: a tap was made at 1.5 in. from each end of the winding and another at 5.5 in. from each end, but the latter two taps were not used except for a minor adjustment which will be mentioned later. The winding was covered with Alundum cement, RA 1055, which is a product of the Norton Company.

An additional coil of wire (auxiliary winding) was superimposed on each end of the main winding, and they consisted of five turns wound uniformly over the 1.5 in. end section and then ten more turns for an inch beyond the main winding. This extended the length of tube covered with wire from 18 in. to 20 in. These coils were made with nichrome wire, B. & S. #20, 0.656 ohms per ft.; and the resistance of each coil was 5.9 and 5.8 ohms respectively. The coils were covered with Alundum cement, and their leads were brought to the outside of the furnace.

The end leads of the main winding and the taps at 1.5 in. were brazed to four 1/4 in. diameter iron rods which served as binding posts for the current source and as structural members to hold the transite ends of the furnace and the galvanized iron shell together. The other leads were connected to 1/4 in. brass screws which were bolted to the transite ends.

Both ends of the furnace consisted of two transite discs. The outer discs were 13 in. in diameter and had a 1.5 in. diameter hole in the center; the inner discs were 12 in. in diameter and had a 2 in. diameter hole for the Alundum tube to rest in. The galvanized iron shell of the furnace was made to fit over the two inner transite discs and into grooves in the outer transite discs. Both discs were 1/2 in. thick.

Diatomaceous earth powder was used as an insulator, and considerable difficulty was experienced in getting the insulation uniformly distributed. This is important because the effectiveness of the electrical circuit used to produce a uniform temperature distribution depends on a uniform distribution of insulation. The furnace was insulated by first filling it with diatomaceous earth without any tamping, putting the transite cover on, rolling the furnace over the floor and tapping its side. This caused the insulation to settle horizontally; more insulation was added, and the process was repeated until the settling became negligible. A nickel tube, 18 in. long, 1.5 in. O.D., 1/8 in. wall, was placed in the Alundum tube to aid in distributing the heat uniformly.

The value of the external resistance used in series with the auxiliary coils at the ends of the main winding to produce a uniform temperature zone was approximately 4 ohms. It was not necessary to change this resistance to get a similar temperature distribution over a temperature range of about 100°C, and only the applied potential had to be varied to change the temperature of the furnace.

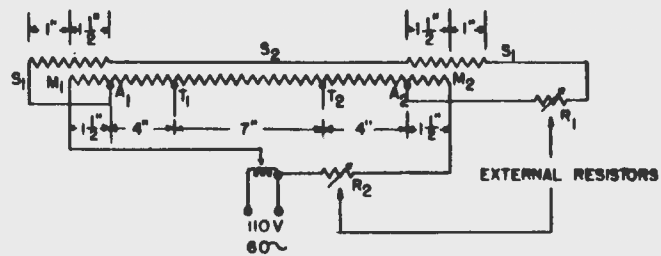
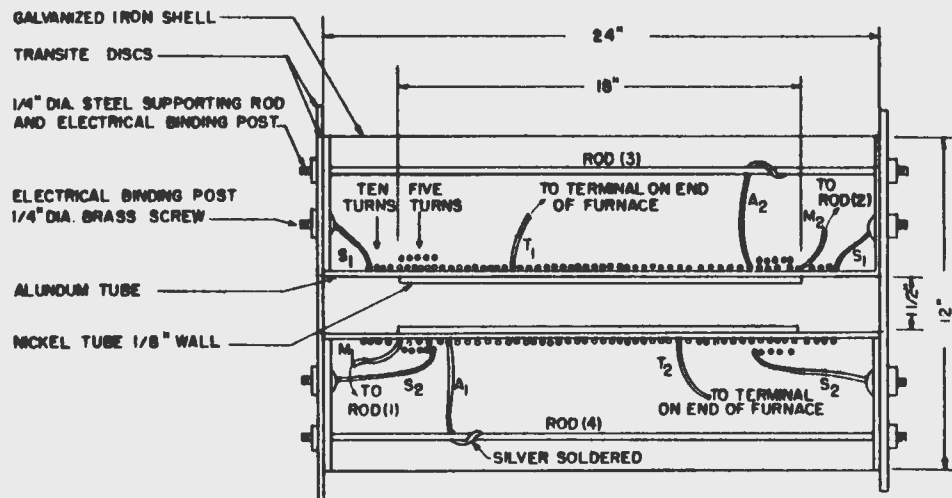


Figure 3. Main Furnace: (Top) Cutaway View,
(Bottom) Electrical Circuit

The temperature distribution along the axis of the furnace for two different temperatures is given in Table 3. An emf of 0.01 mv corresponds to about 1°C. To get the temperature distribution at 720°C a 100 ohm external resistor was connected between the 1.5 in. and the 5.5 in. taps on the right hand side of the furnace to lower a slight maximum which existed there in the data at 790°C.

Table 3
Temperature Distribution in Furnace

Temperature (approx)	Inches from Center of Furnace	Emf in Millivolts	
		Left End	Right End
790°C	1	7.227	7.226
	4	7.227	7.237
	7	7.217	7.224
	8	7.178	7.157
720°C	1	6.427	6.434
	3	6.432	6.435
	5	6.430	6.423
	7	6.428	6.419

8. Thermocouple

A platinum-platinum 10% rhodium thermocouple was used to measure the temperature of the furnace. It was calibrated by determining the emf of the thermocouple at the freezing points of copper, aluminum and zinc. With these values known it was possible to determine the constants of the equation

$$e = a + bt + ct^2,$$

where (t) is the temperature in degrees centigrade and (e) is the emf given by the thermocouple at that temperature. For given values of (t), corresponding values of (e) were obtained from the formula, and a difference plot (difference between the observed emf and the emf given in standard tables at the same temperature versus the observed emf) gave a straight line. The temperature for a given emf was determined by using the plot and standard tables. The metals used for calibration were obtained from the National Bureau of Standards. According to Roeser and Wensel¹¹ the calibration of the thermocouple by the above procedure is accurate to 0.6°C within the temperature range of the freezing points of zinc and copper.

9. Analytical system - Figure 4

This system consists of a Urry type automatic Toepler pump (1000 cc capacity), which was purchased from Wakefield Industries, a gas storage bulb, a mercury manometer, a copper oxide combustion tube, and a small trap which was immersed in liquid nitrogen to trap out water and carbon dioxide. A compensator was incorporated with the manometer to change the level of the mercury in the pressure side. In this way the calibrated volume (43.0 cm^3) could be reproduced as the gas pressure varied. The inside diameter of the manometer tubes was 1.8 cm, and the heights of the mercury columns were estimated with a cathetometer to 0.01 mm. Before each run the system was evacuated, and the furnace for the copper oxide tube was heated to about 290°C for combustion of hydrogen.

The following procedure was used to analyze for hydrogen and methane. After a run S-7 was closed, the mercury level in the pressure side of the manometer was adjusted to a height which was used in calibrating the volume of the storage section and the pressure and temperature of the gases were determined. A liquid nitrogen bath was placed under T_5 , the mercury level on the pressure side of the manometer was raised to the capillary tubing, S-9 and S-8 were opened, and the gas mixture (hydrogen + methane) was circulated with the Toepler pump through the heated copper oxide tube for about ten minutes, which corresponded to about 10-15 strokes of the pump. After this, S-9 was closed, and the unburned gas was pumped back into the storage section for a pressure measurement. Before the pressure could be measured the mercury level had to be changed to its original position. The decrease in pressure was that due to the combustion of hydrogen. For the combustion of methane the temperature of the copper oxide tube was increased to about 870°C , the liquid nitrogen bath was replaced by a carbon dioxide-alcohol bath and methane was circulated through the copper oxide tube as before. While the copper oxide was being heated to 870°C S-8 was closed to prevent unnecessary decomposition of copper oxide. Otherwise the oxygen would have expanded into the large volume of the Toepler pump thereby requiring a considerable evolution of oxygen before reaching its equilibrium pressure. After about fifteen minutes of circulation the furnace was turned off, the carbon dioxide bath was changed to liquid nitrogen bath to trap out carbon dioxide and the gases were circulated continuously to make the oxygen recombine with copper until the furnace cooled to about 400°C . Then S-9 was closed and the uncombined oxygen was pumped into the storage bulb for a pressure measurement; this pressure ranged from 0.05 mm to about 0.2 mm of mercury. After this the liquid nitrogen bath was again changed to a carbon dioxide bath and the carbon dioxide from the combustion of methane was pumped into the storage section to be measured. Analyses of known mixtures of hydrogen (99.8 mole percent purity) and methane (99 mole percent purity) are given below. To determine the amount of condensed gases (C_2 hydrocarbons and others) obtained during the run, S-8 was closed, S-7 was opened, the liquid nitrogen bath under T_4 was changed to a carbon dioxide bath and the gases were pumped into the storage bulb to be measured. They were then analyzed in the same way as methane.

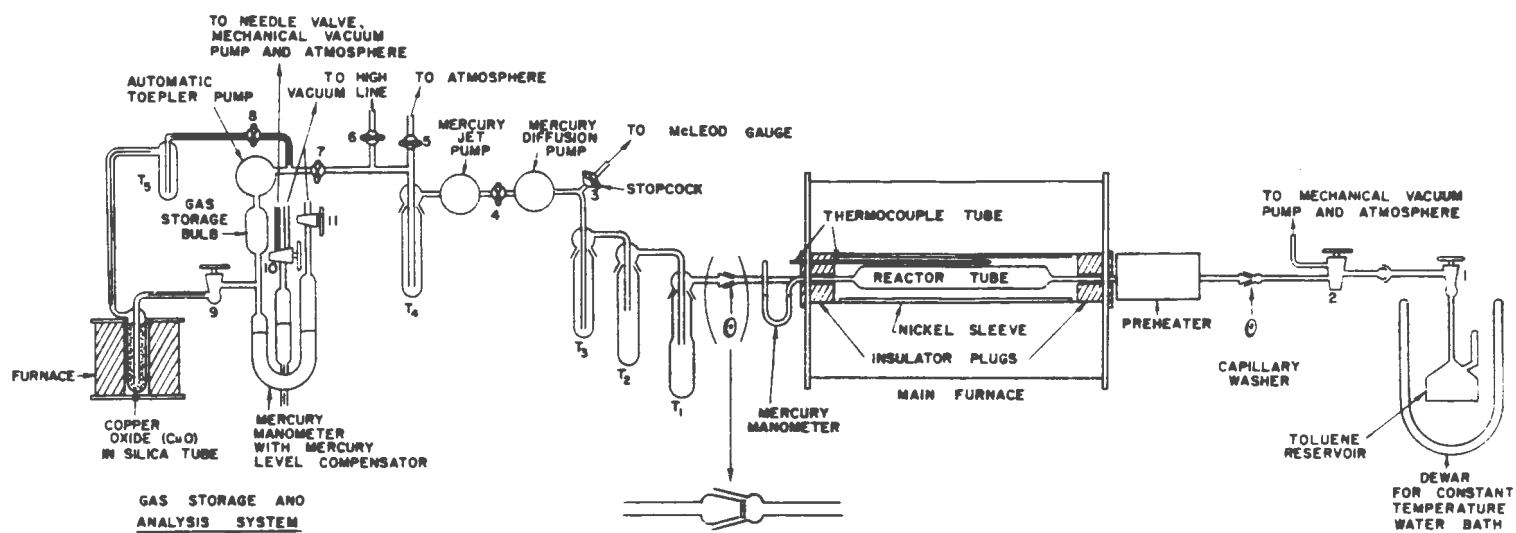


Figure 4. Pyrolysis Apparatus

Table 4

Fractional Combustion of H_2 in $(H_2 + CH_4)$ Mixtures

Run	Pressure in mm of Hg			CH_4 after Combustion of H_2
	H_2	$H_2 + CH_4$	CH_4	
1	6.12	9.96	3.84	3.88
2	6.11	12.90	6.79	6.77

B. Operating Procedure

While a batch of toluene is being outgassed and transferred to the toluene reservoir, S-2 and S-5 are closed and all the others are opened except S-3 which is always closed except when a pressure measurement is desired. The entire system is then evacuated and the main furnace is turned on. About 30-40 hours is required for the furnace to reach temperature equilibrium. After the toluene reservoir has been filled it is weighed and attached to the pyrolysis apparatus; S-2 is then opened to the system to evacuate the tubing connecting the stopcock with the reservoir, and the water bath for the reservoir is prepared. The night before a run is made the copper oxide furnace is turned on, and several hours before a run the preheater and mercury diffusion pumps are turned on. When the main furnace has reached temperature equilibrium and the pressure of the system is 10^{-5} mm of mercury or less, S-9 and S-8 are closed, a carbon dioxide bath is placed under T_1 and liquid nitrogen baths are placed under T_3 and T_4 ; S-6 is closed, S-1 is opened and the automatic Toepler pump is set into operation. When a sufficient amount of gas has been collected S-1 is closed, the preheater is turned off and the system is continuously pumped for about ten minutes after which S-7 is closed. The liquid nitrogen bath under T_3 is next changed to a carbon dioxide bath to transfer C_2 and C_3 hydrocarbons into T_4 . After about ten minutes S-4 is closed, the carbon dioxide bath is changed to a liquid nitrogen bath and the mercury diffusion pump but not the jet pump, is turned off. After the gases have been analyzed S-2 is turned to admit air into the tubing between it and the reservoir, and the reservoir is weighed to determine the amount of toluene used. The section devoted to the analytical system described the method for analyzing the C_2 and C_3 hydrocarbons. When this has been done the mercury jet pump is shut off. In preparation for another run the voltage to the main furnace is changed for a new temperature equilibrium, the reservoir which can hold a sufficient amount of toluene for about 3-4 runs is again connected to the apparatus and the carbon dioxide bath under T_1 is changed to a liquid nitrogen bath to prevent vacuum distillation of toluene until the next run is ready to be made. One day was usually sufficient for the furnace to reach its new temperature

equilibrium. After the toluene from the reservoir was exhausted the liquid contents of T_1 were distilled into T_2 . (See section on traps.) The solids remaining in T_1 were weighed, and the undecomposed toluene was fractionally distilled to remove benzene and any solids and high boiling compounds which were not separated by the vacuum distillation.

C. Derivation of the Rate Constant

The expression used for calculating the rate constant was formulated by Harris¹², and it may be derived in the following way for the case of negligible diffusion of reactants and products. For the reaction (assumed to be first order)

$$A = nC$$

let

N_{Ao} = number of moles of reactant (A) entering the reactor per second

N_A, N_C = number of moles of reactant (A) and products (C) leaving the reactor per second

V_o = velocity of flow of entering mixture in liters/second

V_r = volume of reaction chamber

n = number of moles of product formed per mole of a given reactant undergoing reaction

t = contact time.

In each element of reaction space the rate of reaction is given by

$$\frac{dN_A}{dt} = -k_1 N_A \quad (13)$$

The volume occupied by the mixture of reactants and products at any time, assuming they act as ideal gases, is

$$V = \frac{RT}{P}(N_A + N_C)$$

but

$$\begin{aligned} N_A(\text{at any time}) &= N_{Ao} - (\text{number of moles of A used to form C}) \\ &= N_{Ao} - (1/n)N_C \end{aligned} \quad (14)$$

and

$$V = \frac{RT}{P} \left[N_{A0} + \frac{(n-1)}{n} N_C \right], \quad (15)$$

The symbols T and P are the temperature and pressure of the gases in the reaction zone, and V defines the volume of mixture which passes through any sectional plane of the reactor in a unit time. Next consider the volume of the reacting mixture to pass through an element of volume, dV_r , of the reaction chamber. Its time in the volume element of the reactor is

$$dt = \frac{dV_r}{V}. \quad (16)$$

With the use of equation (16)

$$\frac{dN_A}{dt} = \frac{dN_A}{dV_r} \frac{dV_r}{dt} = \frac{V dN_A}{dV_r}, \quad (17)$$

but from equations (13) and (17)

$$-k_1 A = \frac{V dN_A}{dV_r}. \quad (18)$$

Differentiation of (14) with respect to V_r and substitution of the resulting equation and equations (14) and (15) into (18) yields

$$(1/n) \frac{dN_C}{dV_r} = k_1 \frac{P}{RT} \left[\frac{N_{A0} - (1/n) N_C}{N_{A0} + (n-1/n) N_C} \right]. \quad (19)$$

Integration of (19) with the condition that $N_C = 0$ when $V_r = 0$ yields

$$k_1 = \frac{RT}{PV_r} \left[n N_{A0} \ln \frac{N_{A0}}{N_{A0} - (1/n) N_C} - \frac{(n-1)}{n} N_C \right],$$

but for an ideal gas

$$\frac{N_{A0} RT}{P} = V_0,$$

and

$$k_1 = \frac{V_0}{V_r} \left[n \ln \frac{N_{A0}}{N_{A0} - (1/n) N_C} - \frac{(n-1)}{n} \frac{N_C}{N_{A0}} \right].$$

If there is no volume change; i.e., $n = 1$ and

$$N_C \ll N_{A0}$$

and

$$k_1 = \frac{V_o}{V_r} \ln \frac{N_{A0}}{N_{A0} - N_C} = \frac{V_o}{V_r} \left[\frac{N_C}{N_{A0}} + \frac{1}{2} \left(\frac{N_C}{N_{A0}} \right)^2 + \dots \right]$$

The ratio

$$\frac{V_o}{V_r} = \frac{1}{t},$$

and k becomes

$$k_1 = \frac{1}{t} \frac{N_C}{N_{A0}} \quad (20)$$

RESULTS

Runs III, IV, V, and VI in that order were made with toluene x325 which was purchased from Eastman Kodak Company. These runs are indicated by squares in Figure 5. This toluene was used without any preliminary purification; after each run it was vacuum distilled from one trap into another to remove the solid products formed and used as such for succeeding runs. A considerable amount of carbon was formed in run III, and in order to avoid this runs IV, V and VI were made with higher rates of flow. The layer of carbon was thicker toward the outlet of the reactor tube than at the inlet, and the amount formed decreased with increasing rates of flow and decreasing temperature. Only a negligible amount of carbon formed in run VI; the larger rate constant obtained in this run as compared to run V cannot be explained readily; unless the formation of carbon means a loss of hydrogen and methane. (See Table 5.) It should be noted that run VI was made at a relatively low pressure which suggests that carbon formation might be eliminated by simply reducing the pressure sufficiently without using high rates of flow.

The remaining runs (identified by circles) were made with research grade toluene (99.89 mole percent purity) from Phillips Petroleum Company. Before runs VII to XV were made the toluene was pyrolyzed twice at 850°C and distilled over calcium hydride after each pyrolysis. Runs XVI, XVII, and XVIII were made with toluene used in runs VII to XV after pyrolyzing it twice more at 850°C and combining it with toluene which had been previously pyrolyzed three times at 850°C. There appears to be no appreciable difference in rates between the two groups of runs due to additional pre-pyrolysis treatments.

Table 5
Results of Toluene Pyrolysis

Run	Temp. °K	Average Pressure in mm of Hg	Contact Time in Seconds	Fraction Decomposed x10 ⁵	kx10 ⁵	% CH ₄
VII	976	9.6	0.316	1.82(?)	5.76	47 ^a
VIII	978	13.1	0.322	2.77	8.60	43
XVIII	995.5	13.0	0.320	6.04	18.9	40.4
XVI	996	13.1	0.320	3.17(?)	9.90	44-46 ^a
XI	1001	14.3	0.326	7.57	23.3	41.1
IX	1016	12.9	0.312	13.5	43.2	42.4
XII	1024	9.4	0.306	18.2	59.5	38.6
X	1030	12.4	0.290	22.1	76.2	38.5
XV	1047	11.3	0.134	16.7	124	41.3
XIII	1051	7.3	0.0598	7.62	128	42 ^b
XVII	1063(?)	13.0	0.300	64.2	215	36.7
XIV	1068	~ 7.8	0.0625	16.7	267	38 ^c
IV	1077	7.7	0.126	38.6	303	34.5
V	1088	5.1	0.0590	30.6	519	36.8
VI	1088	3.3	0.0358	23.6	659	35.9
III	1092	15.2	0.299	196.	656	36.0

^a This probably includes nitrogen which has leaked into the apparatus during the run.

^b On the basis of combustion of hydrogen alone the percentage of methane was 45.6%. After methane was burned and the carbon dioxide pressure measured, more carbon dioxide was found than could be accounted for by methane alone. The percentage of methane given in the table was calculated on the basis that the additional carbon dioxide came from ethene which did not condense in the liquid nitrogen trap.

^c A similar situation as (b) above. The percentage of methane on basis of combustion of H₂ was ~40%.

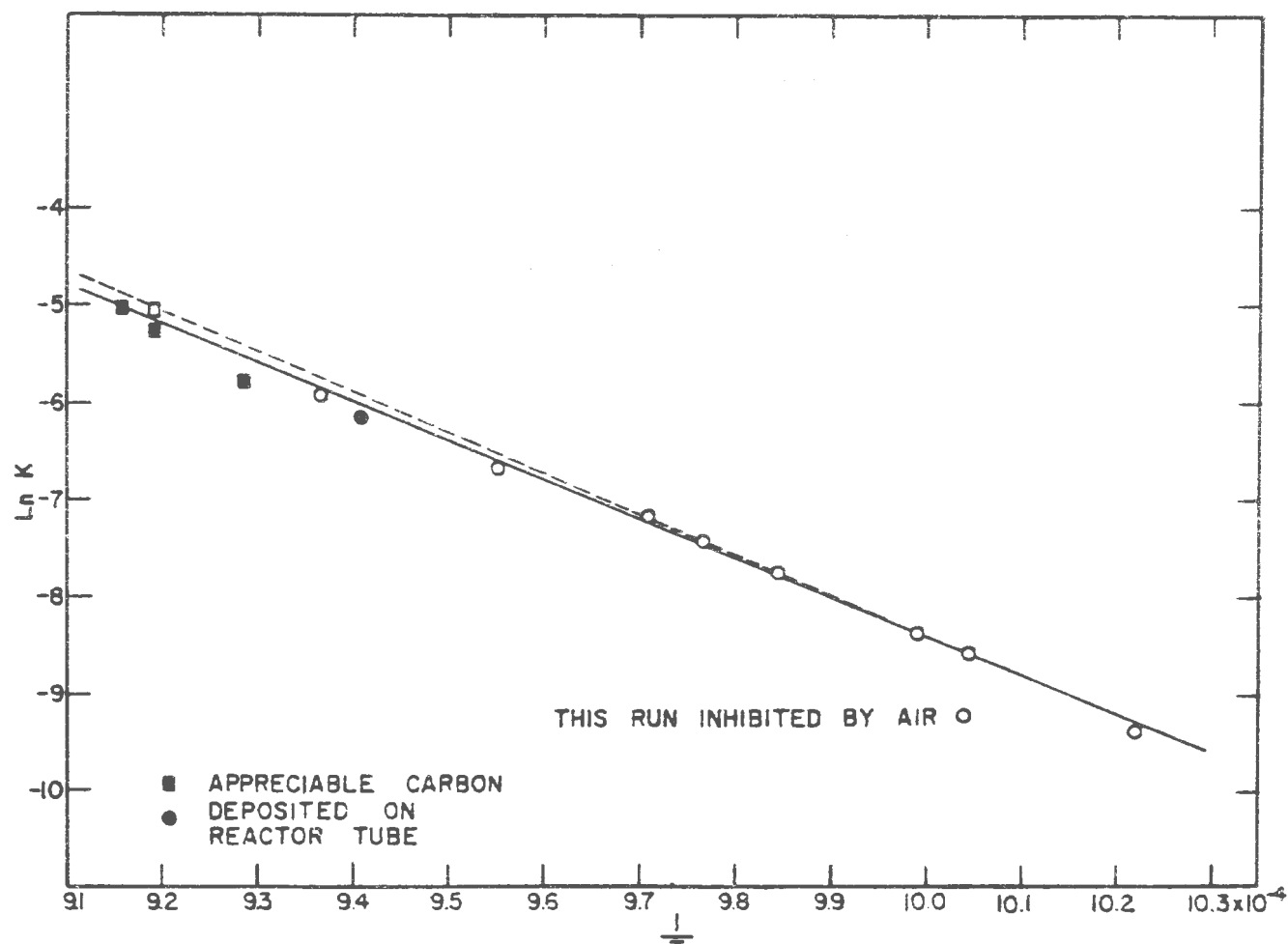


Figure 5. Temperature Dependence of Rate Constant
for Pyrolysis of Toluene

Runs VII to XVIII may be grouped into sets according to the amount of toluene available to make a given number of runs. After each set of runs the toluene was fractionally distilled over calcium hydride to remove solid products and benzene; the resulting toluene then formed another batch for the second set of runs and so on. Thus runs VII, VIII, IX, and X belong to one set, XI and XII to a second set, XIII and XIV to a third set, XV to a fourth and XVI, XVII and XVIII to a fifth set.

Run XIII was made with a high rate of mass flow which caused the furnace to cool down about 2°C during the run; the low rate constant obtained for that run was attributed to the inability of the toluene to achieve temperature equilibrium immediately upon entering the reactor tube. The rate constant should be compared with that of run XV which was done at a lower temperature, a slower rate of flow and increased heat input of the preheater. For this reason run XIII was excluded from the data used for an estimation of the activation energy. No decomposition of toluene occurred as a result of preheating. This was determined by sending toluene through the reactor tube with the preheater being the only source of heat and measuring the amount of gas given off, if any, for a period of about an hour.

Run XVI was included in the graph to show inhibition by air which had leaked into the apparatus during the run. The amount of air leak was extremely small since the total amount of gas, hydrogen, methane, carbon dioxide and nitrogen, was not much more than the hydrogen and methane obtained in run XVIII which was made at approximately the same temperature. (See Table 8 in appendix.) The rate constant for run XVI is half as large as that obtained in run XVIII. In run VII a relatively large amount of condensable gas, presumably carbon dioxide, was obtained; thus, the run was suspected of being inhibited by air and was not included in the graph and the data for calculating the activation energy.

Run XVII was made to deposit a layer of carbon on the reactor tube, and runs XVI and XVIII were made at a lower temperature prior to and after this run respectively to determine the effect of carbon on the rate of decomposition. Unfortunately run XVI was inhibited by air and a direct comparison could not be made, but by comparing run XVIII with other points which fall on a line one can see that carbon had very little effect on the rate.

Table 5 shows that the percentage composition of methane in the non-condensable gases is not constant but decreases with increasing temperature. This is somewhat consistent with the other investigators since Szwarc observed approximately 40% methane and H. Blades, A. Blades and Steacie observed approximately 31% methane. These percentages were constant within experimental limits throughout the temperature ranges in which they worked. In this research the percentage of methane ranged from about 42% in the low temperature region to about 36% in the high temperature region. After runs

VII to XV were made gas samples for a mass spectrographic analysis were taken and the results showed the presence of small amounts of ethene, propene, carbon dioxide and perhaps propyne. A quantitative estimate of each of these was not made. The rate of production of these compounds did not seem to vary much with temperature. Szwarc did not observe any C₂ hydrocarbons, and H. Blades, A. Blades and Steacie obtained C₂ and C₃ hydrocarbon in the first pyrolysis; but these disappeared after the second or third pyrolysis. On the other hand, Schaeffer¹³ obtained C₂, C₃ and C₄ hydrocarbons in the pyrolysis of p-xylene and attributed their presence to wall effects. It should be mentioned that the number of moles (assuming molecular weight of dibenzyl) of solid products found was always less than the number of moles of hydrogen plus methane. In several cases the amount was much closer to that of methane. H. Blades, A. Blades and Steacie found similar results. Figures 6 and 7 show the ultra-violet spectra of pure dibenzyl and of solid decomposition products of toluene in methanol. The exact concentrations of the two solutions are unknown but the former is more concentrated than the latter. The difference between the two is suspected of being due to the presence of a compound containing a diphenyl nucleus. H. Blades, A. Blades and Steacie suggested the presence of isomers of dimethyl diphenyl. No attempt was made to isolate the compounds.

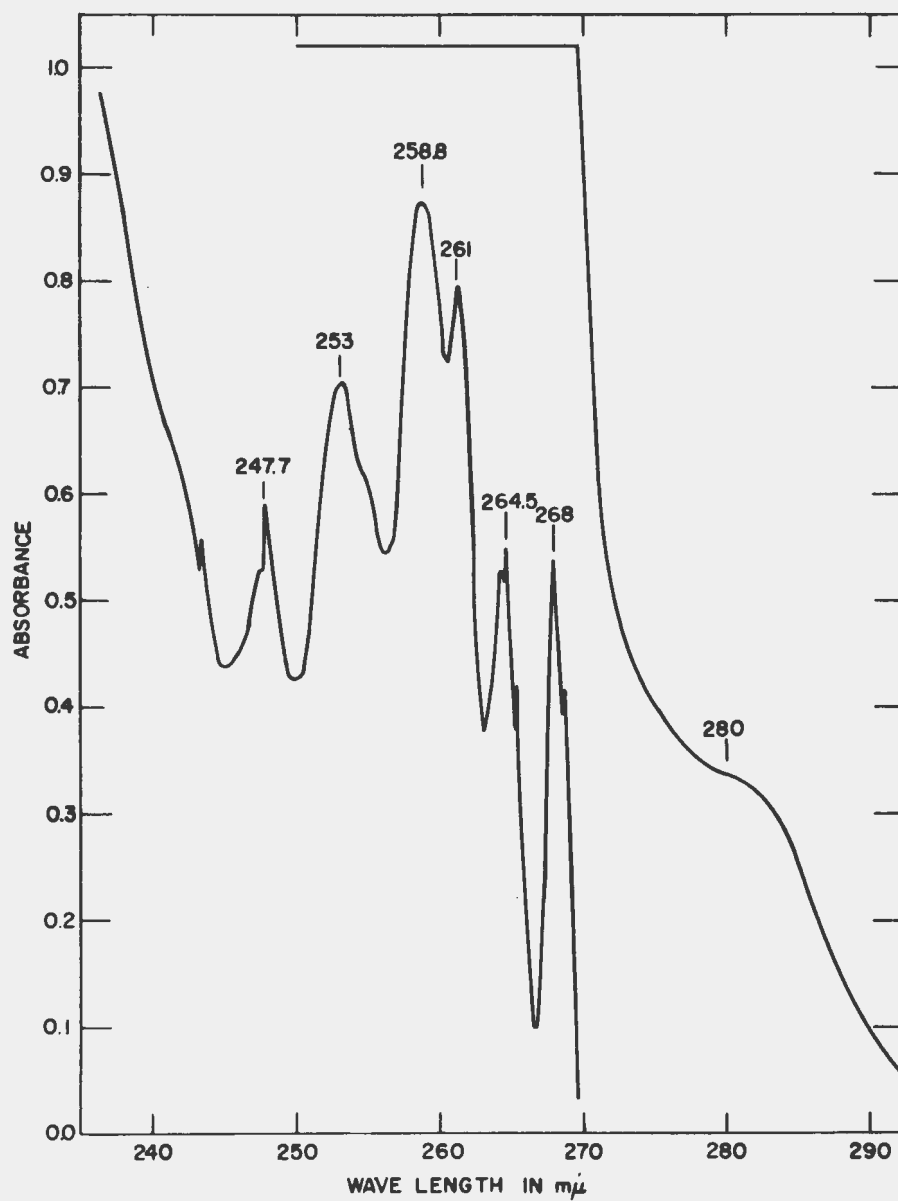


Figure 6. Ultraviolet Spectra of Pure
Dibenzyl in Methanol

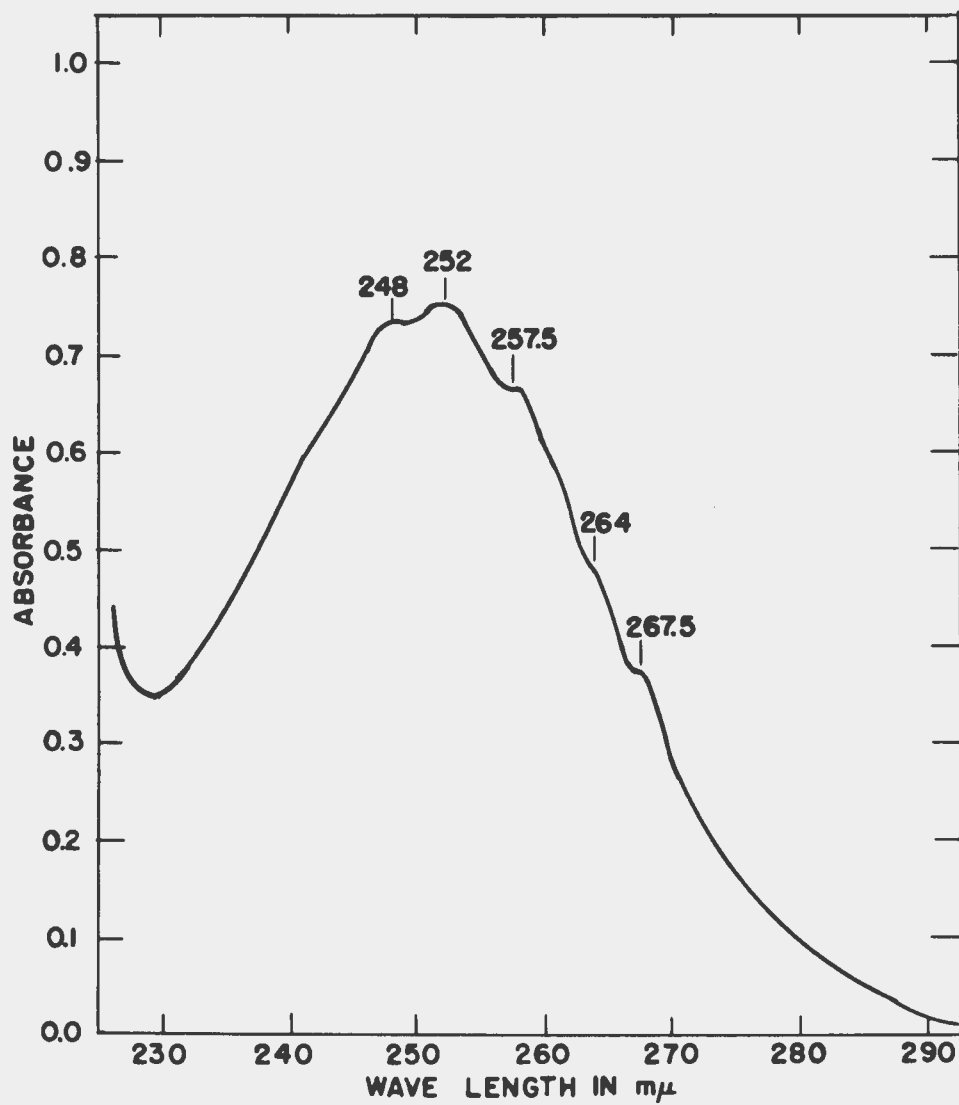


Figure 7. Ultraviolet Spectra of Solid Decomposition Products of Toluene in Methanol

DISCUSSION

A plot of $\ln k$ (k = reaction rate constant) versus the reciprocal temperature is given in Figure 5. Except for the run inhibited by air all the points on the graph are best represented by the solid line as determined by the method of least squares. Its equation is

$$\ln k = - \frac{3.94 \times 10^4}{T} + 31.0$$

which yields an activation energy of 78.3 kcal/mole. Similarly the dashed line represents those points between 978°K and 1030°K and yields an activation energy of about 84 kcal/mole. Figure 8 shows how this line and the points on it compare with Szwarc's data. It is seen that they agree quite well.

It seems improper to consider indiscriminately those runs which resulted in carbon formation and those which were performed at high rates of flow with those runs which resulted in a negligible amount or no carbon formation and were performed at low rates of flow. At high rates of flow there is less opportunity for the gas to reach temperature equilibrium with the furnace so that the rate constants derived from those runs are expected to be low. Likewise if the formation of carbon is associated with the loss of methane and hydrogen (compare runs V and VI) those runs which result in carbon formation are expected to be low. Under those assumptions more weight should be given to the low temperature points, but the question arises as to how much weight. This is unknown, and all that can be said is that the activation energy resides between 78 and 84 kcal/mole. At this point it should be made clear that Szwarc neglected his first four low temperature points in calculating the activation energy. If these are included the energy increases to about 81-82 kcal/mole. In any event the mechanism for the decomposition of toluene should be proven before any activation energy can be assigned to a dissociation energy.

Hentz and Burton's results indicate that $D(\phi\text{CH}_2\text{-H})$ is probably less than $D(\phi\text{-CH}_3)$ because only a small amount of methane was produced. (See Historical section.) If this information is used in conjunction with A. Blades and Steacie's work with deuterated toluene there would be little reason to suspect that Szwarc's mechanism is wrong. On the other hand if $D(\phi\text{CH}_2\text{-H})$ and $D(\phi\text{-CH}_3)$ are reasonably close one must question whether all of the methane produced is derived from the rupture of the (C-H) bond.

The results of this research indicate that $D(\phi\text{-CH}_3) \leq D(\phi\text{CH}_2\text{-H})$. Actually a least mean square of the points in the plots of $\ln k$ versus $1/T$ for production of hydrogen alone and for methane alone yields activation energies of 81.5 and 76 kcal/mole respectively. If the rate constants from runs VI and XVIII are used only the activation energies become 84.2 kcal/mole for hydrogen and 79.8 kcal/mole for methane. On the basis of this one would expect to get more methane than hydrogen which is contrary to experiment. The k values for production of hydrogen and methane may be found in the appendix.

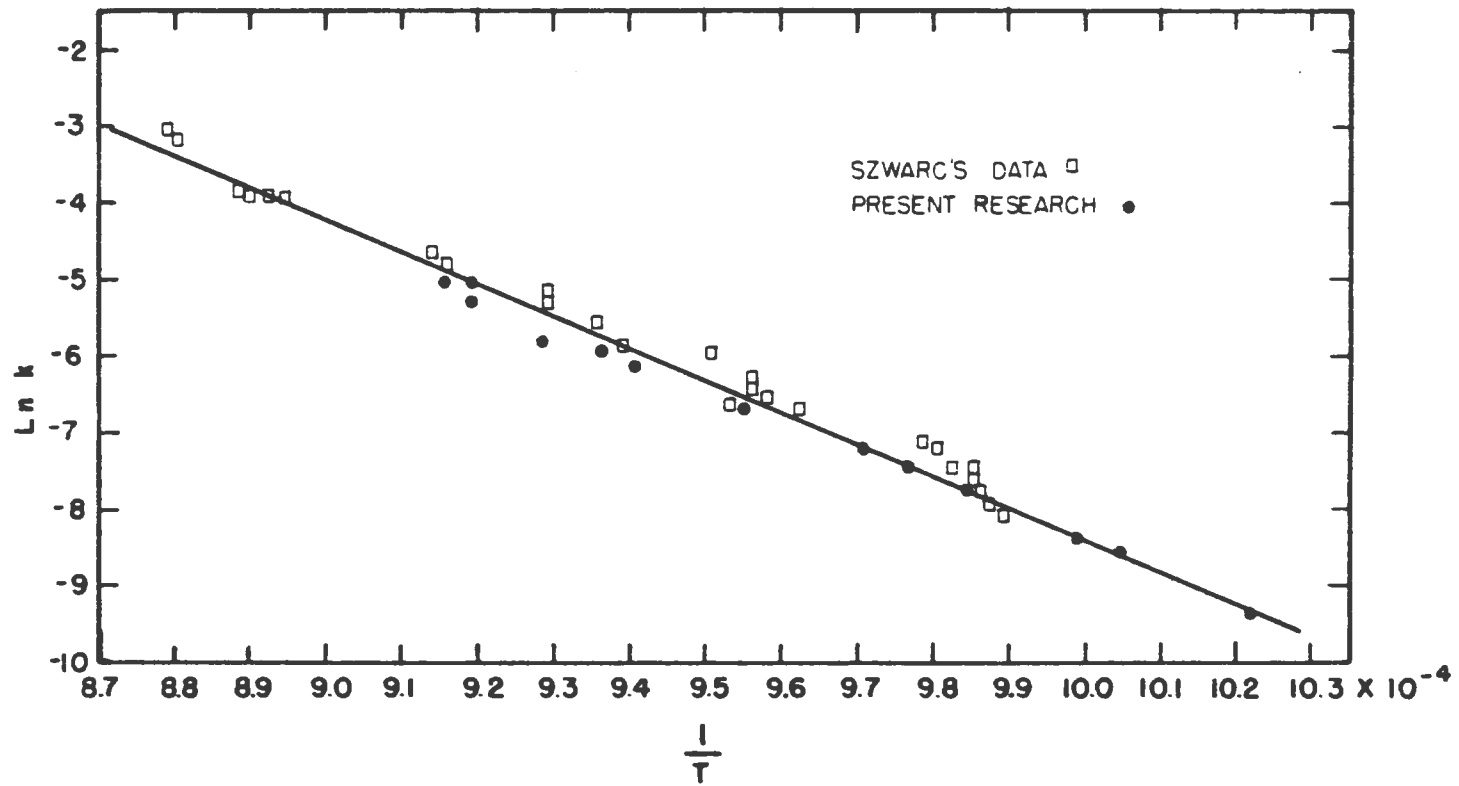


Figure 8. Comparison of Szwarc's Data with Present Research

The (C-C) bond distance between the methyl groups and the benzene ring in mesitylene and p-xylene have been given by Pauling¹⁴. These distances are about 0.01 Å to 0.02 Å shorter than the (C-C) bond distance in ethane. The dissociation energy of the (C-C) bond in ethane is about 84 kcal/mole. Thus it seems unlikely that this bond ruptures in toluene; unless, the phenyl radical possesses a reorganization energy or resonance energy much greater than the methyl radical.

Evidence opposing Szwarc's mechanism is found in the heat of formation of bromobenzene. Two values for this quantity exist; given these values, and $D(\phi\text{-Br})$ it is possible to calculate two values for $D(\phi\text{-CH}_3)$ which are 80.9 and 86 kcal/mole. There is evidence in favor of the higher value for the heat of formation of bromobenzene and therefore the higher value for the dissociation energy. All this assumes, of course, that $D(\phi\text{-Br})$, which was determined by Szwarc by the pyrolysis of bromobenzene in the presence of toluene, is correct.

Pauling¹⁵ has suggested that if the bond in a molecule (A-B) is purely covalent, the dissociation energy is given by

$$D(A-B) = \frac{1}{2} [D(A-A) + D(B-B)] \quad (21)$$

where A and B are atoms. In many molecules, however, the bonds are not purely covalent, and the above equation does not apply. The deviations from the above equation have been used to formulate an electronegativity scale of the elements.

In the present work, use has been made of the above equation (extended to the case where A and B are radicals) to predict carbon-carbon bond dissociation energies in organic molecules, and it has been extended to predict dissociation energies of bonds which involve a carbon atom and a hetero-atom (e. g., $D(\text{CH}_3\text{-H})$) by the adoption of a concept called the group potential, which may be defined in the following way

$$D(A-B) = GP(A) + GP(B) \quad (22)$$

where $GP(A)$ is the group potential of fragment A. The solution of equation (22) is made unique by defining $GP(A)$, where A is the group which contributes the carbon atom to the bond, by

$$GP(A) = \frac{1}{2} D(A-A).$$

This is equivalent to the first term on the right hand side of equation (21). Once $GP(A)$ has been established from a symmetrical organic molecule, $GP(B)$ must be found from equation (22) and cannot be determined like $GP(A)$; otherwise, the result would be equivalent to (21) which was found not to apply. Having found $GP(B)$, one is able to use this value to predict other dissociation energies; or, alternatively, this value may be used to predict the group potential of a group, A, for which the dissociation energy of the symmetrical

molecule is not available. Equation (22) actually incorporates empirically such effects as electronegativity, and the concept of group potential is analogous to the average bond energy except that it is applied to a fragment and its ability to form a bond. It appears that the fragments having the higher group potentials are more reactive; therefore, they are a measure of the stability or reactivity of the various groups. Some group potentials and predicted dissociation energies are tabulated in Tables 6 and 7.

An extreme example will illustrate how the results of equations (21) and (22) differ. By equation (21),

$$\begin{aligned} D(\text{CH}_2:\text{CHCH}_2\text{-OH}) &= D(\text{CH}_2:\text{CHCH}_2\text{-CH}_3) - \frac{1}{2}D(\text{CH}_3\text{-CH}_3) + \frac{1}{2}D(\text{HO-OH}) \\ &= 61.5 - 42 + 27 \\ &= 46.5, \end{aligned}$$

by equation (22),

$$\begin{aligned} D(\text{CH}_2:\text{CHCH}_2\text{-OH}) &= \text{GP}(\text{CH}_2:\text{CHCH}_2\text{-}) + \text{GP}(\text{OH}) \\ &= 25 + 48 \\ &= 73, \end{aligned}$$

experimentally,

$$D(\text{CH}_2:\text{CHCH}_2\text{-OH}) = 71.$$

Table 6

Derived Group Potentials

Compound	Dissociation Energy of Bond	Group	Group Potential
$\text{CH}_3\text{-CH}_3$	84	CH_3	42
$\text{CH}_3\text{-H}$	102	H	60
$\text{CH}_3\text{-Br}$	67	Br	$67-42=25$
$\text{CH}_3\text{-I}$	53	I	11
$\text{CH}_3\text{-NH}_2$	80	NH_2	38
$\text{CH}_3\text{-SH}$	70	SH	28
$\text{CH}_3\text{-SCH}_3$	73	SCH_3	31
$\text{CH}_3\text{-OH}$	90	OH	48
$\text{CH}_3\text{-CHO}$	75	CHO	33
$\text{CH}_3\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{-CH}_3$	72	$\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{-CH}_3$	30
$\text{CH}_3\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{-}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{CH}_3$	60	$\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{-CH}_3$	$60/2=30$
$n\text{-C}_3\text{H}_7\text{-H}$	100	$n\text{-C}_3\text{H}_7$	$100-60=40$
iso. $\text{C}_3\text{H}_7\text{-H}$	94	iso. C_3H_7	34
tert. $\text{C}_4\text{H}_9\text{-H}$	89	tert. C_4H_9	29
neo. $\text{C}_5\text{H}_{11}\text{-H}$	95	neo. C_5H_{11}	35
$\text{CCl}_3\text{-H}$	89	CCl_3	29
$\text{CBr}_3\text{-H}$	93	CBr_3	33
$\text{C}_2\text{H}_5\text{-H}$	96	C_2H_5	36
$\phi\text{-Br}$	71	ϕ	$71-25=46$
$\text{CH}_2\text{:CHCH}_2\text{-I}$	36	$\text{CH}_2\text{:CH-CH}_2$	25
$\phi\text{CH}_2\text{-OH}_2\phi$	47	ϕCH_2	$47/2=23$

Table 7

Predicted and Observed Dissociation Energies

Compound	Bond Dissociation Energy	
	Predicted	Observed
$\phi\text{CH}_2\text{-H}$	83	77.5
$\phi\text{CH}_2\text{-NH}_2$	61	59
$\phi\text{CH}_2\text{-Br}$	48	51
$\phi\text{CH}_2\text{-I}$	34	39
$\phi\text{CH}_2\text{-CH}_3$	65	63
$\phi\text{CH}_2\text{-}\overset{\text{O}}{\parallel}\text{CCH}_3$	53	63
$\phi\text{CH}_2\text{-SCH}_3$	54	51.5
$\text{C}_2\text{H}_5\text{-Br}$	61	—
$\text{C}_2\text{H}_5\text{-I}$	47	51
$n\text{C}_3\text{H}_7\text{-I}$	51	50
iso. $\text{C}_3\text{H}_7\text{-I}$	45	46
tert. $\text{C}_3\text{H}_7\text{-I}$	40	45(?)
$\text{CH}_2\text{:CHCH}_2\text{-Br}$	50	46
$\text{CH}_2\text{:CHCH}_2\text{-CH}_3$	67	61.5
$\text{CH}_2\text{:CHCH}_2\text{OH}$	73	71
$\text{CH}_2\text{:CHCH}_2\text{-H}$	85	77
$\phi\text{-I}$	57	57
$\phi\text{-H}$	106	102
$\text{CCl}_3\text{-Br}$	54	52 or 59

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Table 8

Additional Data from Pyrolysis of Toluene

Run	Moles $H_2 + CH_4$ $\times 10^6$	Moles Toluene	Duration of Run Sec.	Rate of Flow		Moles $H_2 \times 10^6$	$k \times 10^5$ (H_2)	Moles $CH_4 \times 10^6$	$k \times 10^5$ (CH_4)
				$\frac{\text{Moles}}{\text{Sec.}}$ $\times 10^5$	$\frac{\text{Ml.}}{\text{Sec.}}$				
VIII	8.85	0.31979	5355	5.972	278	5.05	4.90	3.80	3.69
XVIII	17.0	0.28086	4800	5.851	280	10.1	11.3	6.85	7.64
XI	20.0	0.26439	4205	6.287	275	11.8	13.7	8.22	9.56
IX	22.7	0.16849	2880	5.850	288	13.1	24.9	9.60	18.3
XII	36.1	0.19826	4611	4.300	293	22.2	36.5	13.9	23.0
X	46.2	0.20973	3518	5.962	309	28.4	46.9	17.8	29.3
XV	36.8	0.22027	1912	11.52	666	21.6	73.1	15.2	51.4
XVII	68.0	0.10585	1805	5.864	299	43.0	136	25.0	78.9
XIV	42.4	0.25388	1510	16.81	1433	25.1 ^a	158	16.2	102
IV	74.4	0.19304	2402	8.037	704	48.7	199	25.7	105
V	84.0	0.27445	2401	11.43	1518	53.1	328	30.9	191
VI	64.6	0.27347	2280	11.99	2496	41.4	422	23.2	237
III	105	0.05348	800	6.682	299	67.2	420	37.8	236

^a The number of moles of hydrogen and methane is somewhat uncertain because the mixture probably contained hydrocarbons other than methane.